Fungicidal active compound combinations

The present invention relates to novel active compound combinations which comprise the known 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione and further known fungicidally active compounds, and which are highly suitable for controlling phytopathogenic fungi.
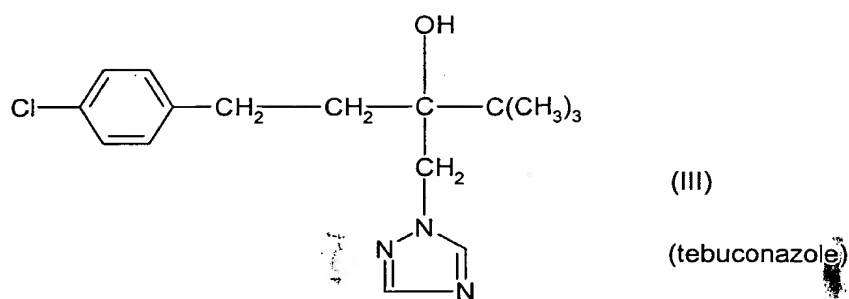
It is already known that 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione has fungicidal properties (cf. WO 96-16 048). The activity of this compound is good; however, at low application rates it is in some cases not satisfactory.

Furthermore, it is already known that a large number of triazole derivatives, aniline derivatives, dicarboximides and other heterocycles can be employed for controlling fungi (cf. EP-A 0 040 345, DE-A 2 201 063, DE-A 2 324 0 10, Pesticide Manual, 9th Edition (1991), pages 249 and 827, US-A 3 903 090 and EP-A 0 206 999). Likewise, the activity of these compounds is not always satisfactory at low application rates.

Finally, it is also known that 1-[(6-chloro-3-pyridinyl)-methyl]-N-nitro-2-imidazolidineimine can be used for controlling animal pests such as insects (cf. Pesticide Manual, 9th Edition (1991), page 491). However, fungicidal properties have not hitherto been described for this compound.
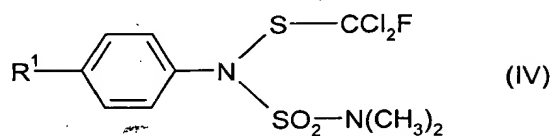
It has now been found that the novel active compound combinations comprising

2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione of the formula

$$Cl\text{—}C_6H_4\text{—}CH_2\text{—}CH_2\text{—}\underset{\underset{CH_2}{|}}{\overset{\overset{OH}{|}}{C}}\text{—}C(CH_3)_3$$

(III)

(tebuconazole)

and/or

(3)   an aniline derivative of the formula

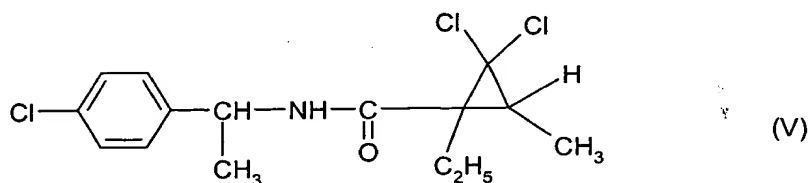$$R^1\text{—}C_6H_4\text{—}\underset{\underset{SO_2\text{—}N(CH_3)_2}{}}{\overset{\overset{S\text{—}CCl_2F}{}}{N}}$$

(IV)

in which

R^1 represents hydrogen or methyl,

and/or

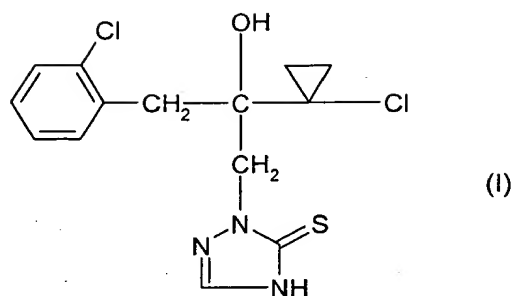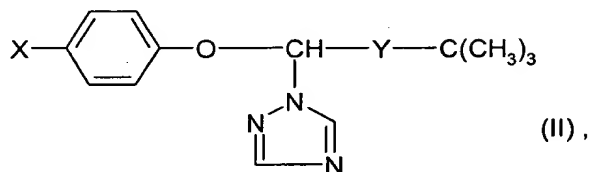(4)   N-[1-(4-chloro-phenyl)-ethyl]-2,2-dichloro-1-ethyl-3-methyl-cyclopropane-carboxamide of the formula

$$Cl\text{—}C_6H_4\text{—}\underset{\underset{CH_3}{|}}{CH}\text{—}NH\text{—}\underset{\underset{O}{\|}}{C}\text{—}\text{(cyclopropane ring: Cl, Cl, H, CH}_3\text{, }C_2H_5\text{)}$$

(V)

and/or

(5)   the zinc propylene-1,2-bis-(dithiocarbamidate) of the formula

$$\text{2-Cl-C}_6\text{H}_4\text{—CH}_2\text{—}\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle N}{|}}{C}}(\triangle)\text{—Cl}$$

(I)

and

5 (1) a triazole derivative of the formula

$$X\text{—}\langle\text{C}_6\text{H}_4\rangle\text{—O—CH—Y—C(CH}_3)_3$$

(II) ,

in which

10

X represents chlorine or phenyl

and

Y represents $-\overset{\overset{\displaystyle O}{\|}}{C}-$ or $-\overset{\overset{}{\underset{\underset{\displaystyle OH}{|}}{CH}}}-$,

15

and/or

(2) the triazole derivative of the formula

20
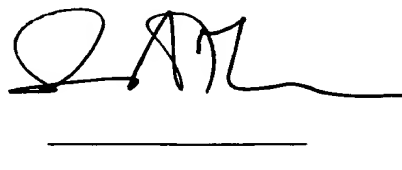
UNITED STATES PATENT AND TRADEMARK OFFICE

I, Susan ANTHONY BA, ACIS,

Director of RWS Group Ltd, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1.   That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.

2.   That the translator responsible for the attached translation is well acquainted with the German and English languages.

3.   That the attached is, to the best of RWS Group Ltd knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in the Germany on 18 April 1997 under the number 197 16 257.6 and the official certificate attached hereto.

4.   That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.
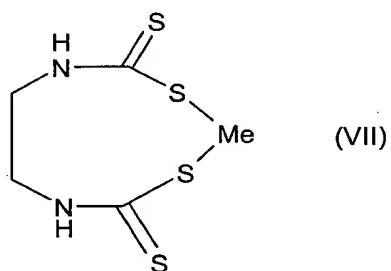
For and on behalf of RWS Group Ltd

The 28th day of March 2006

$$n >= 1 \qquad \text{(propineb)}$$
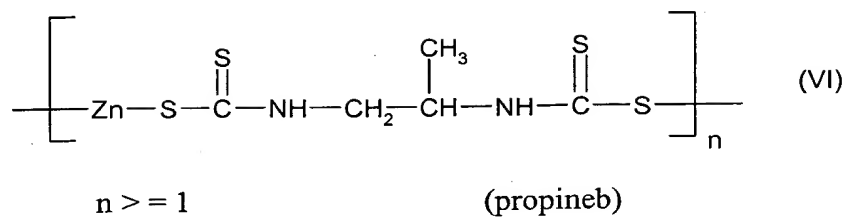
5 and/or

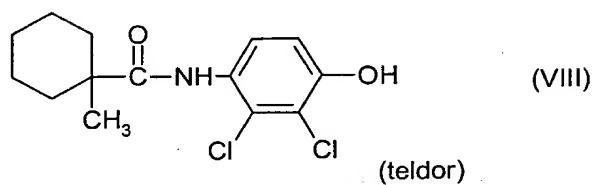(6) at least one thiocarbamate of the formula

(VII)

10

Me = Zn or Mn
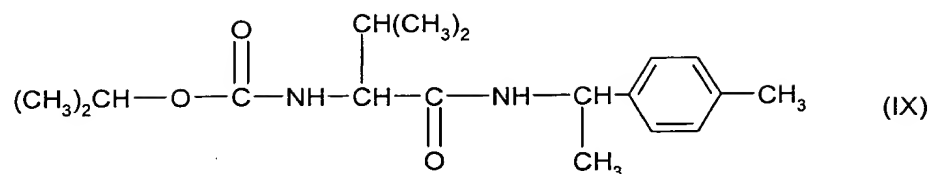
or a mixture of Zn and Mn

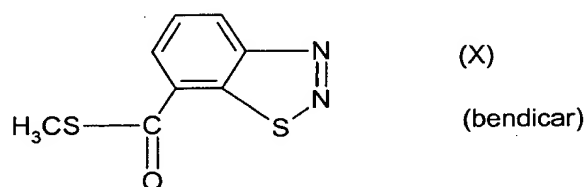and/or

15

(7) the aniline derivative of the formula

(VIII)
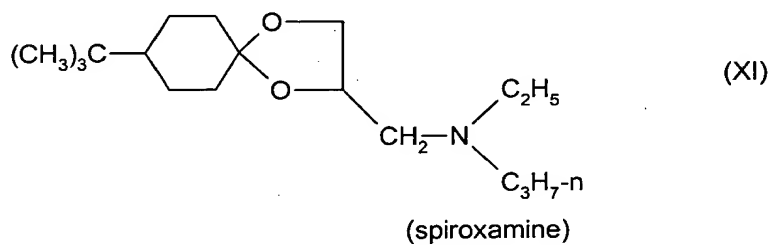
(teldor)

20 and/or

(8) the compound of the formula

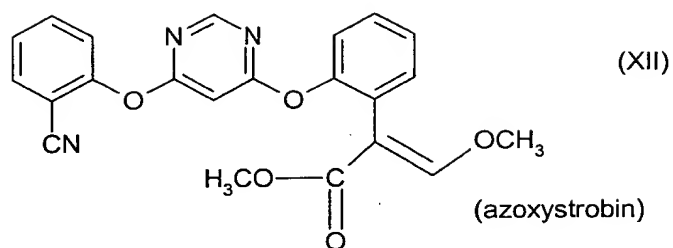(IX)

and/or

(9)   the benzothiadiazole derivative of the formula

(X)

(bendicar)

and/or

(10)   the   8-t-butyl-2-(N-ethyl-N-n-propyl-amino)-methyl-1,4-dioxaspiro-
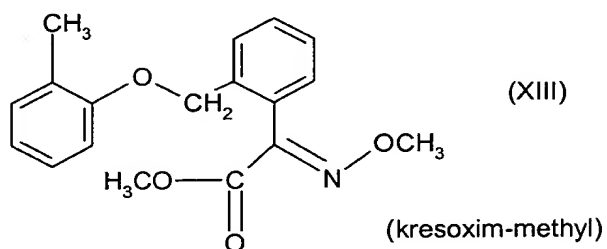   [5,4]-decane of the formula

(XI)

(spiroxamine)

and/or

(11)   the compound of the formula

(XII)

(azoxystrobin)

and/or

(12)   the compound of the formula

(XIII)

(kresoxim-methyl)

and/or

(13)   the compound of the formula

(XIV)

and/or

(14)   the dicarboximide of the formula

(XV)

(procymidone)
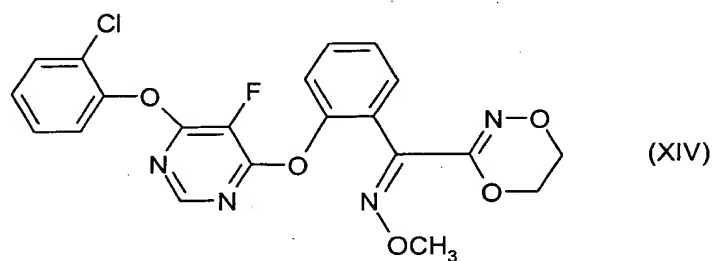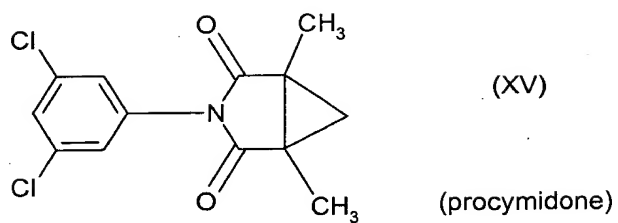
and/or

5 (15) a pyrimidine derivative of the formula

(XVI)
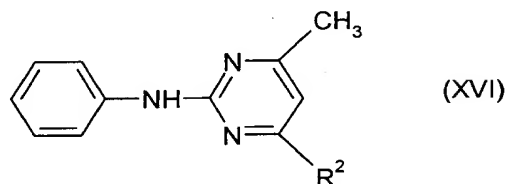
in which

10 R^2 represents methyl or cyclopropyl,
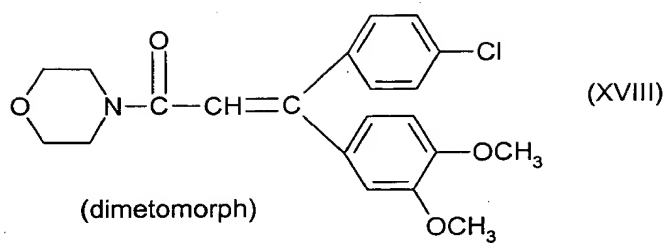
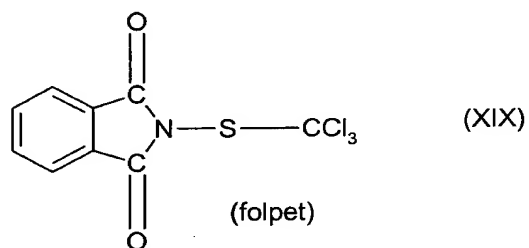and/or

15 (16) the phenyl derivative of the formula

(XVII)

(chlorothalonil)
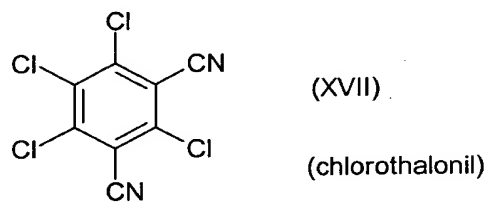
and/or

20

(17) the morpholine derivative of the formula

(dimetomorph)   (XVIII)

and/or

5   (18)   the phthalimide derivative of the formula
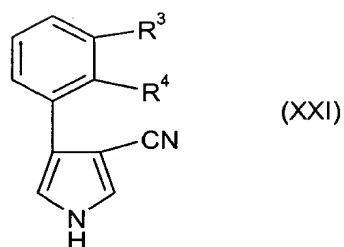

(folpet)   (XIX)

and/or

10

(19)   the phosphorus compound of the formula
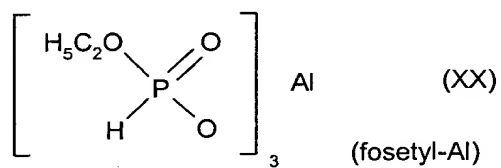
(fosetyl-Al)   (XX)

and/or

15   and/or
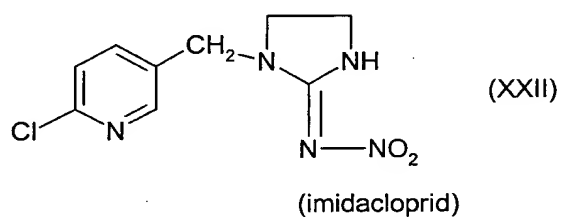
(20)   a phenylpyrrole derivative of the formula

(XXI)

in which

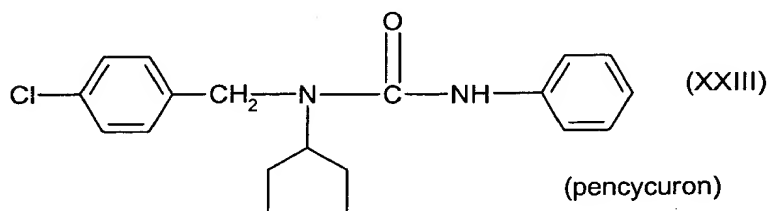R³ and R⁴ each represent chlorine or together represent a radical of the formula -O-CF$_2$-O-,

and/or

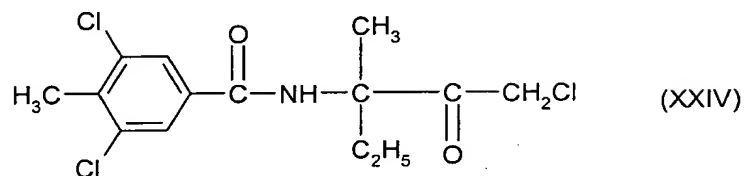(21) the 1-[(6-chloro-3-pyridinyl)-methyl]-N-nitro-2-imidazolidineimine of the formula

(XXII)

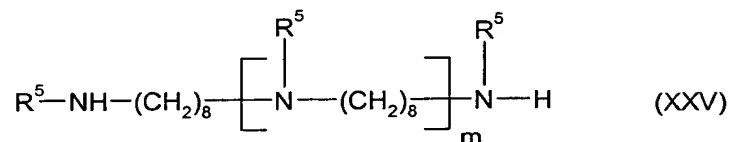(imidacloprid)

and/or

(22) the phenylurea derivative of the formula

(XXIII)

(pencycuron)

and/or

(23) the benzamide derivative of the formula

$$\underset{Cl}{\overset{Cl}{\underset{|}{\bigcirc}}}H_3C-\overset{Cl}{\underset{Cl}{\bigcirc}}-\overset{O}{\overset{\|}{C}}-NH-\overset{CH_3}{\underset{C_2H_5}{\overset{|}{C}}}-\overset{O}{\underset{\|}{C}}-CH_2Cl \qquad (XXIV)$$

and/or

(24) a guanidine derivative of the formula

$$R^5-NH-(CH_2)_8-\left[\overset{R^5}{\underset{}{\overset{|}{N}}}-(CH_2)_8\right]_m\overset{R^5}{\underset{}{\overset{|}{N}}}-H \qquad (XXV)$$

$$x \ (2 + m) \ CH_3COOH$$

in which

m   represents integers from 0 to 5

and

R^5 represents hydrogen (17 to 23 %) or the radical of the formula

$$-\overset{}{\underset{NH_2}{\overset{|}{C}}}=NH \qquad (77 \text{ to } 83 \text{ %}),$$
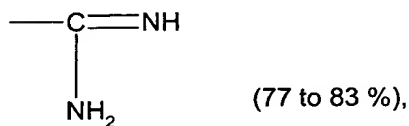
have very good fungicidal properties.

Surprisingly, the fungicidal activity of the active compound combinations according to the invention is considerably higher than the sum of the activities of the individual

active compounds. Thus, an unforeseeable, true synergistic effect is present, and not

just an addition of activities.

5   The   2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-
[1,2,4]-triazole-3-thione of the formula (I) is known (cf. WO 96-16 048). The
compound can be present in the „thiono" form of the formula

(I)
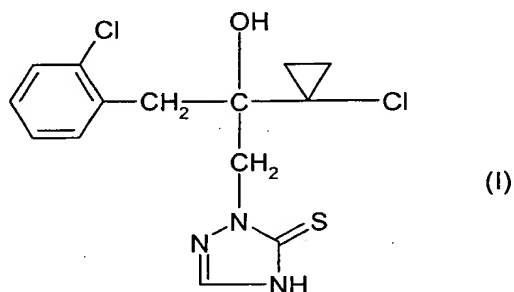
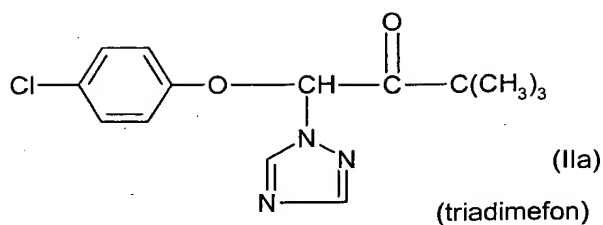10   or in the tautomeric „mercapto" form of the formula

(Ia).
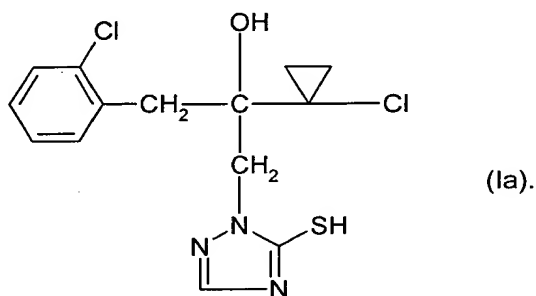
For simplicity's sake, only the „thiono" form is given in each case.

15
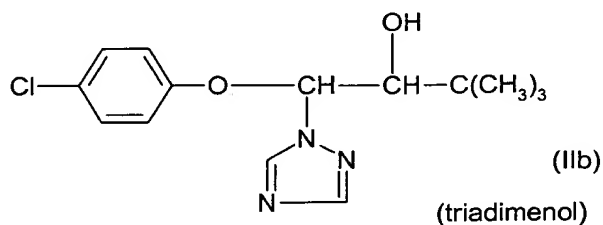
The formula (II) includes the compounds

1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-butane-2-one of the formula

20

(IIa)

(triadimefon)

1-(4-chloro-phenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-butan-2-ol of the formula
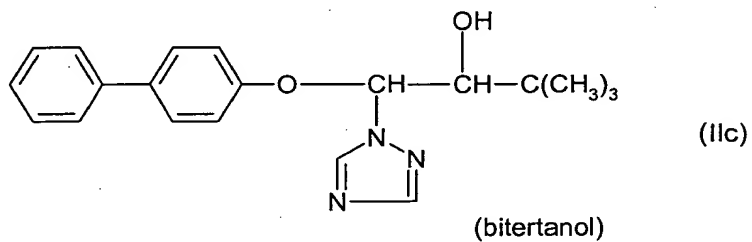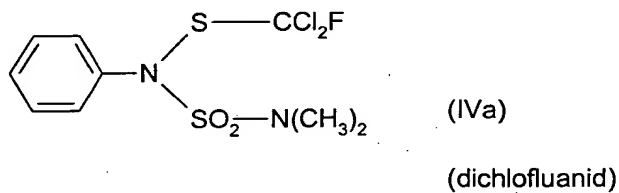

(IIb)

(triadimenol)

and

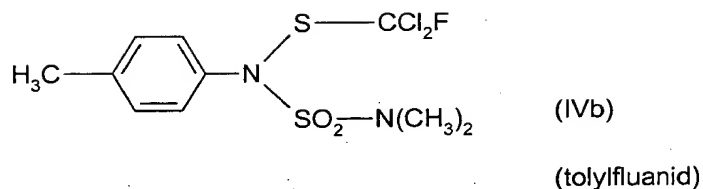1-(4-phenyl-phenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)-butan-2-ol of the formula

(IIc)

(bitertanol)

The formula (IV) includes the aniline derivatives of the formulae

(IVa)

(dichlofluanid)

and

$$H_3C-\bigcirc-N\begin{smallmatrix}S-CCl_2F\\SO_2-N(CH_3)_2\end{smallmatrix}$$ (IVb)
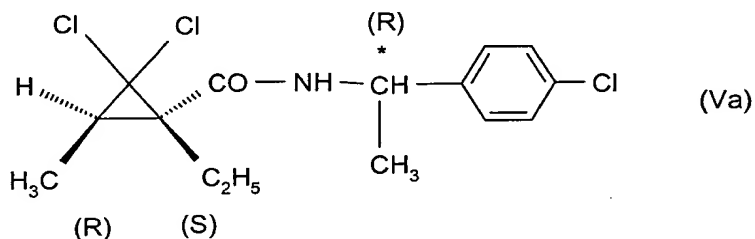
(tolylfluanid)

It is evident from the formula for the active compound of the formula (V) that the
5 compound has three asymmetrically substituted carbon atoms. The product may
therefore be present as a mixture of various isomers, or else in the form of a single
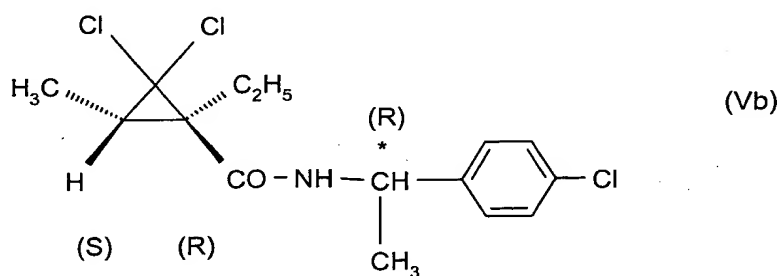component. Particular preference is given to the compounds

N-(R)-[1-(4-chloro-phenyl)-ethyl]-(1S)-2,2-dichloro-1-ethyl-3t-methyl-1r-
10 cyclopropanecarboxamide of the formula

(Va)

and

15

N-(R)-[1-(4-chloro-phenyl)-ethyl]-(1R)-2,2-dichloro-1-ethyl-3t-methyl-1r-
cyclopropanecarboxamide of the formula

(Vb)

20

The formula (VII) includes the compounds

(VIIa)   Me = Zn   (zineb)

(VIIb)   Me = Mn   (maneb)

5   and

(VIIc)   mixture of (VIIa) and (VIIb) (mancozeb).

The formula (XVI) includes the compounds

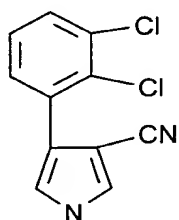10   (XVIa) R^2 = CH$_3$ (pyrimethanil)

and

(XVIb) R^2 =   (cyprodinyl)

The formula (XXI) includes the compounds

15

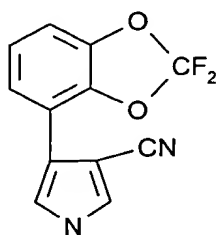4-(2,3-dichlorophenyl)-pyrrole-3-carbonitrile of the formula

(XXIa)

(fenpiclonil)

20   and

4-(2,2-difluoro-1,3-benzodioxol-7-yl)-1H-pyrrole-3-carbonitrile of the formula

(XXIb)

(fludioxonil)

The guanidine derivative of the formula (XXV) is a mixture of substances of the common name guazatine.

The components which are present in the active compound combinations according to the invention in addition to the active compound of the formula (I) are also known. Specifically, the active compounds are described in the following publications:

(1)   Compounds of the formula (II)

DE-A 2 201 063

DE-A 2 324 010

(2)   Compound of the formula (III)

EP-A 0 040 345

(3)   Compounds of the formula (IV)

Pesticide Manual, 9th Edition (1991), pages 249 and 827

(4)   Compound of the formula (V) and individual isomers thereof

EP-A 0 341 475

(5)   Compound of the formula (VI)

Pesticide Manual, 9th Edition (1991), pages 726

(6)   Compounds of the formula (VII)

Pesticide Manual, 9th Edition (1991), pages 529, 531 and 866

(7)   Compound of the formula (VIII)

EP-A 0 339 418

(8)   Compound of the formula (IX)

EP-A 0 472 996

(9)   Compound of the formula (X)

          EP-A 0 313 512

(10)   Compound of the formula (XI)

5   EP-A 0 281 842

(11)   Compound of the formula (XII)

          EP-A 0 382 375

10   (12)   Compound of the formula (XIII)

          EP-A 0 515 901

(13)   Compound of the formula (XIV)

          EP-A 196 02 095

15

(14)   Compound of the formula (XV)

          US-A 3 903 090

(15)   Compounds of the formula (XVI)

20   EP-A 0 270 111

          EP-A 0 310 550

(16)   Compound of the formula (XVII)

          Pesticide Manual, 9th Edition (1991), page 159

25

(17)   Compound of the formula (XVIII)

          EP-A 0 219 756

(18)   Compound of the formula (XIX)

30   Pesticide Manual, 9th Edition (1991), page 431

(19)   Compound of the formula (XX)

Pesticide Manual, 9th Edition (1991), page 443

(20)   Compounds of the formula (XXI)

EP-A 0 236 272

5   EP-A 0 206 999

(21)   Compound of the formula (XXII)

Pesticide Manual, 9th Edition (1991), page 491

10 (22)   Compound of the formula (XXIII)

DE-A 2 732 257

(23)   Compound of the formula (XXIV)

EP-A 0 600 629

15

(24)   Substance of the formula (XXV)

Pesticide Manual, 9th Edition (1991), page 461

In addition to the active compound of the formula (I), the active compound

20 combinations according to the invention comprise at least one active compound of
the compounds of groups (1) to (24). Additionally, they may comprise further
fungicidally active components.

The synergistic effect is particularly pronounced when the active compounds in the

25 active compound combinations according to the invention are present in certain
weight ratios. However, the weight ratios of the active compounds in the active
compound combinations can be varied within a relatively wide range. In general,

0.1 to 20 parts by weight, preferably 0.2 to 10 parts by weight, of active compound of

30 group (1),

0.1 to 20 parts by weight, preferably 0.2 to 10 parts by weight, of active compound of group (2),

0.2 to 150 parts by weight, preferably 1 to 100 parts by weight, of active compound
5   of group (3),

0.1 to 10 parts by weight, preferably 0.2 to 5 parts by weight, of active compound of group (4),

10   1 to 50 parts by weight, preferably 5 to 20 parts by weight, of active compound of group (5),

1 to 50 parts by weight, preferably 2 to 20 parts by weight, of active compound of group (6),

15

0.1 to 50 parts by weight, preferably 1 to 30 parts by weight, of active compound of group (7),

0.2 to 50 parts by weight, preferably 1 to 20 parts by weight, of active compound of
20   group (8),

0.02 to 50 parts by weight, preferably 0.2 to 10 parts by weight, of active compound of group (9),

25   0.1 to 50 parts by weight, preferably 0.2 to 20 parts by weight, of active compound of group (10),

0.1 to 50 parts by weight, preferably 0.2 to 20 parts by weight, of active compound of group (11),

30

0.1 to 50 parts by weight, preferably 0.2 to 20 parts by weight, of active compound of group (12),

0.1 to 50 parts by weight, preferably 0.2 to 20 parts by weight, of active compound of group (13),

5   0.1 to 50 parts by weight, preferably 1 to 30 parts by weight, of active compound of group (14),

0.1 to 50 parts by weight, preferably 0.2 to 20 parts by weight, of active compound of group (15),

10

0.1 to 50 parts by weight, preferably 2 to 20 parts by weight, of active compound of group (16),

1 to 20 parts by weight, preferably 2 to 10 parts by weight, of active compound of

15   group (17),

1 to 50 parts by weight, preferably 2 to 20 parts by weight, of active compound of group (18),

20   1 to 50 parts by weight, preferably 2 to 20 parts by weight, of active compound of group (19),

0.1 to 10 parts by weight, preferably 0.2 to 5 parts by weight, of active compound of group (20),

25

0.05 to 20 parts by weight, preferably 0.1 to 10 parts by weight, of active compound of group (21),

0.1 to 10 parts by weight, preferably 0.2 to 5 parts by weight, of active compound of

30   group (22),

0.1 to 10 parts by weight, preferably 0.2 to 5 parts by weight, of active compound of group (23),

and/or

5

0.1 to 10 parts by weight, preferably 0.2 to 5 parts by weight, of active compound of group (24)

are present per part by weight of active compound of the formula (I).

10

The active compound combinations according to the invention have very good fungicidal properties and can be employed for controlling phytopathogenic fungi, such as Plasmodiophoromycetes, Oomycetes, Chytridiomycetes, Zygomycetes, Ascomycetes, Basidiomycetes, Deuteromycetes, etc.

15

The active compound combinations according to the invention are particularly suitable for controlling cereal diseases, such as Erysiphe, Puccinia and Fusarium, and for controlling diseases encountered in viticulture, such as Uncinula, Plasmopara and Botrytis, and furthermore in dicotylendonous crops for controlling powdery and

20 downy mildew fungi and causative organisms of leaf spot.

The fact that the active compound combinations are well tolerated by plants at the concentrations required for controlling plant diseases permits the treatment of above-ground parts of plants, of propagation stock and seeds, and of the soil. The active

25 compound combinations according to the invention can be employed for foliar application or else as seed dressings.

The active compound combinations according to the invention can be converted to the customary formulations, such as solutions, emulsions, suspensions, powders,

30 foams, pastes, granules, aerosols and microencapsulations in polymeric substances and in coating compositions for seeds, and ULV formulations.

These formulations are produced in a known manner, for example by mixing the active compounds or active compound combinations with extenders, that is liquid solvents, liquefied gases under pressure, and/or solid carriers, optionally with the use

5   of surfactants, that is emulsifiers and/or dispersants, and/or foam formers. If the extender used is water, it is also possible to use, for example, organic solvents as auxiliary solvents. Essentially, suitable liquid solvents include: aromatics such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride,

10   aliphatic hydrocarbons such as cyclohexane or paraffins, for example petroleum fractions, alcohols such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulphoxide, or else water. Liquefied gaseous extenders or carriers are to be understood as meaning liquids

15   which are gaseous at ambient temperature and under atmospheric pressure, for example aerosol propellants such as butane, propane, nitrogen and carbon dioxide. Suitable solid carriers are: for example ground natural minerals such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals such as finely divided silica, alumina and silicates.

20   Suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks. Suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers, such as

25   polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates, or else protein hydrolysates. Suitable dispersants are: for example lignin-sulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other additives can be

5   mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and prussian blue, and organic dyestuffs such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of

10   iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95% by weight of active compounds, preferably between 0.5 and 90%.

15   In the formulations, the active compound combinations according to the invention can be present as a mixture with other known active compounds such as fungicides, insecticides, acaricides and herbicides, and as mixtures with fertilizers or plant growth regulators.

20   The active compound combinations can be used as such, in the form of their formulations or as the use forms prepared therefrom, such as ready-to-use solutions, emulsifiable concentrates, emulsions, suspensions, wettable powders, soluble powders and granules. They are used in the customary manner, for example by watering, spraying, atomizing, scattering, spreading, and as a powder for dry seed

25   treatment, a solution for seed treatment, a water-soluble powder for seed treatment, a water-soluble powder for slurry treatment, or by encrusting.

When using the active compound combinations according to the invention, the application rates can be varied within a relatively wide range, depending on the kind of application. In the treatment of parts of plants, the application rates of the active compound combination are generally between 0.1 and 10,000 g/ha, preferably

5   between 10 and 1000 g/ha. In the treatment of seeds, the application rates of the active compound combination are generally between 0.001 and 50 g per kilogram of seed, preferably between 0.01 and 10 g per kilogram of seed. In the treatment of the soil, the application rates of the active compound combination are generally between 0.1 and 10,000 g/ha, preferably between 1 and 5000 g/ha.

10

The good fungicidal activity of the active compound combinations according to the invention is evident from the examples below. While the individual active compounds exhibit weaknesses with regard to the fungicidal activity, the combinations have an activity which exceeds a simple addition of activities.

15

A synergistic effect of fungicides is always present when the fungicidal activity of the active compound combinations exceeds the total of the activities of the active compounds when applied individually.

20   The expected activity for a given combination of two active compounds can be calculated as follows (cf. Colby, S.R., "Calculating Synergistic and Antagonistic Responses of Herbicide Combinations", Weeds 15, (1967), 20-22):

If

25

X   is the efficacy when applying active compound A at an application rate of m g/ha,

Y   is the efficacy when applying active compound B at an application rate of $\underline{n}$

g/ha and

5   E   is the efficacy when applying the active compounds A and B at an application

rate of $\underline{m}$ and $\underline{n}$ g/ha,

then

$$E = X + Y - \frac{X \cdot Y}{100}$$

10

The efficacy is calculated in %. 0% is an efficacy which corresponds to that of the

control, whereas an efficacy of 100% means that no infection is observed.

If the actual fungicidal activity exceeds the calculated value, then the activity of the

15 combination is superadditive, i.e. a synergistic effect exists. In this case, the efficacy

which was actually observed must be greater than the value for the expected efficacy

(E) calculated from the abovementioned formula.

The examples that follow illustrate the invention.

Example 1

Sphaerotheca test (cucumber) / protective

5 Solvent: 47 parts by weight of acetone

Emulsifier: 3 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of

10 solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

To test for protective activity, young plants are sprayed with the active compound

15 preparation at the stated application rate. After the spray coating has dried on, the plants are inoculated with an aqueous spore suspension of Sphaerotheca fuliginea. The plants are then placed in a greenhouse at about 23°C and a relative atmospheric humidity of about 70%.

20 Evaluation is carried out 10 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

Active compounds, application rates and test results are shown in the table below.

Table 1

Sphaerotheca test (cucumber) / protective
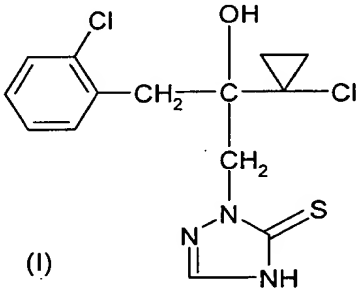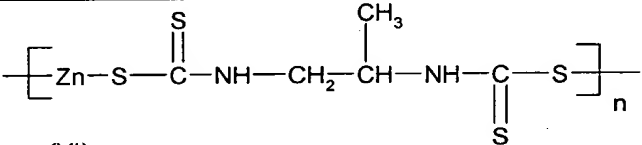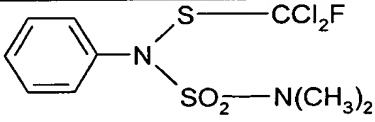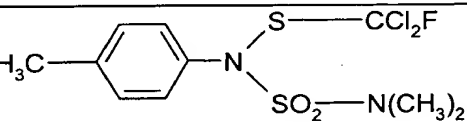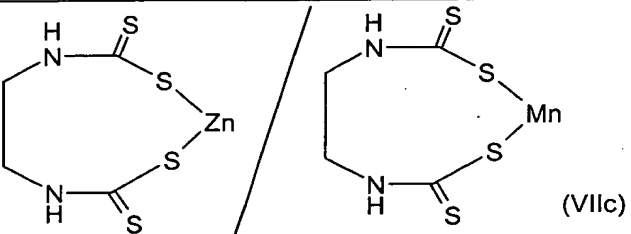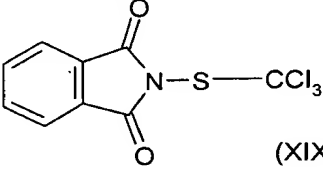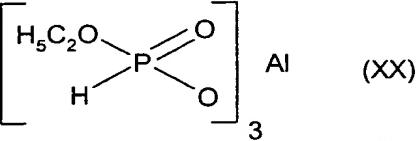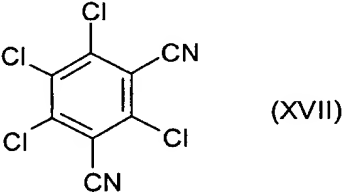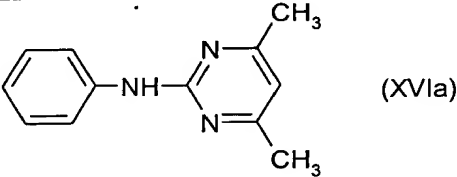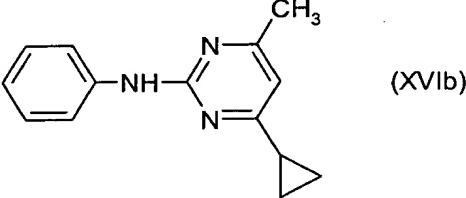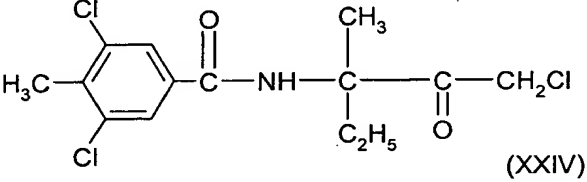
Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I) [chemical structure: 2-chlorobenzyl-C(OH)(cyclopropyl)(Cl)-CH₂-triazole-thione]	2.5 / 0.5	21 / 0
(VI) [Zn–S–C(=S)–NH–CH₂–CH(CH₃)–NH–C(=S)–S]ₙ	25	0
(IVa) [phenyl-N(S–CCl₂F)(SO₂–N(CH₃)₂)]	25	0
(IVb) [H₃C–phenyl-N(S–CCl₂F)(SO₂–N(CH₃)₂)]	25	0
(VIIc) [Zn and Mn bis-dithiocarbamate ring structures]	25	0

5

Table 1 (continued)

Sphaerotheca test (cucumber) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %
(XIX)	25	0
(XX)	50	0
(XVII)	25	0
(XVIa)	25	0
(XVIb)	25	0
(XXIV)	12.5	0

Table 1 (continued)

Sphaerotheca test (cucumber) / protective
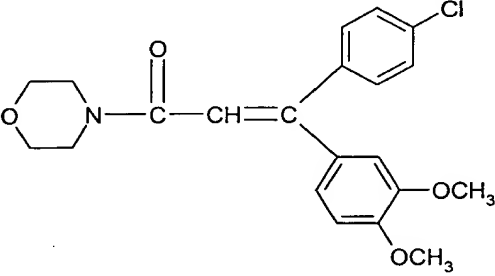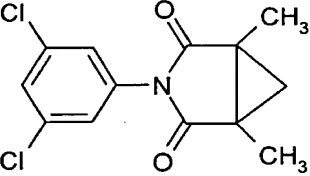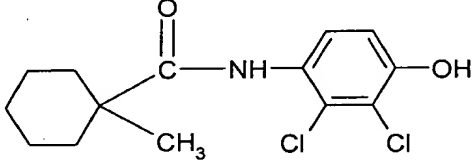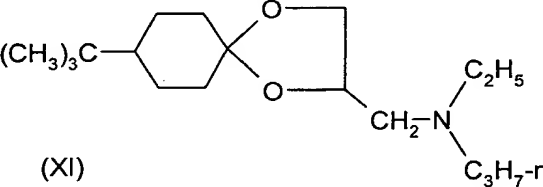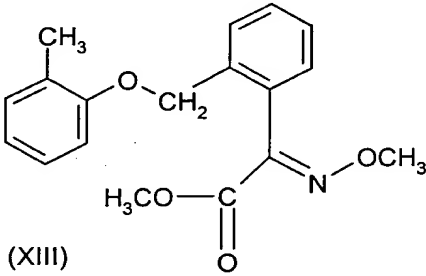
Active compound	Active compound application rate in g/ha	Efficacy in %
(XVIII)	12.5	0
(XV)	12.5	0
(VIII)	12.5	0
(XI)	12.5	0
(XIII)	2.5	57

Table 1 (continued)

Sphaerotheca test (cucumber) / protective
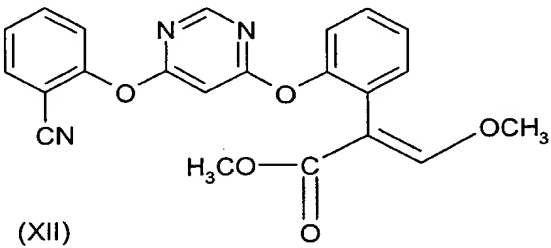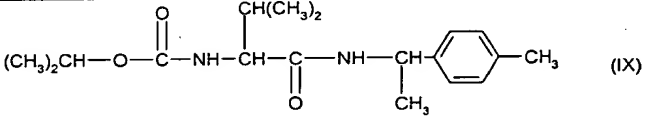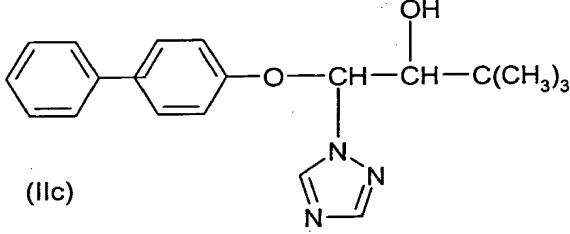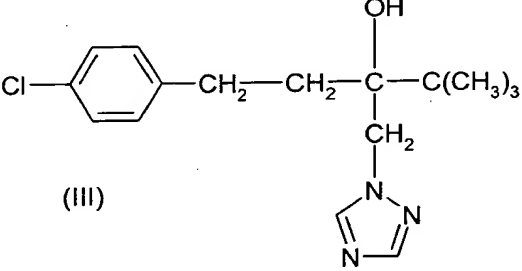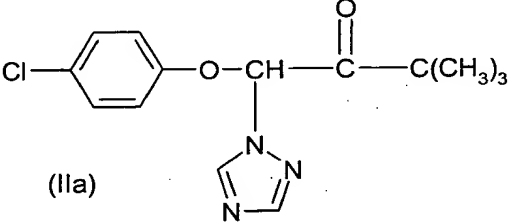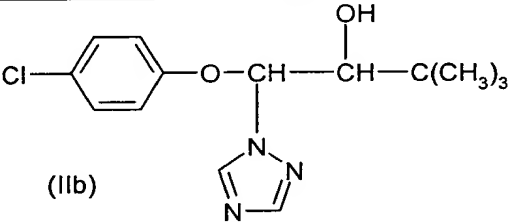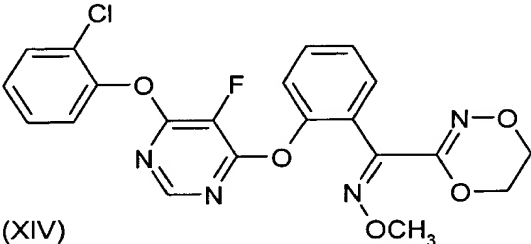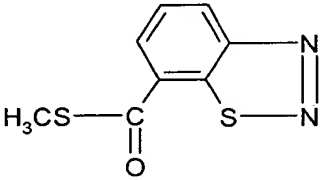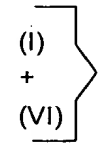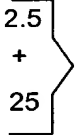
Active compound	Active compound application rate in g/ha	Efficacy in %
(XII)	2.5	59
(IX)	12.5	13
(IIc)	2.5	0
(III)	2.5	50
(IIa)	2.5	37

Table 1 (continued)

Sphaerotheca test (cucumber) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %
(IIb)	2.5	80
(XIV)	2.5	22
(X)	2.5	0
According to the invention: (I) + (VI) (1:10)	2.5 + 25	found calc.*) 70 21

Table 1 (continued)

Sphaerotheca test (cucumber) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %	
(I) + (IVa) (1:10)	2.5 + 25	63	21
		found	calc.*)
(I) + (IVb) (1:10)	2.5 + 25	63	21
(I) + (VIIc) (1:10)	2.5 + 25	63	21
(I) + (XIX) (1:10)	2.5 + 25	59	21
(I) + (XX) (1:20)	2.5 + 50	52	21

Table 1 (continued)

Sphaerotheca test (cucumber) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %	
(I) + (XVII) (1:10)	2.5 + 25	63	21
(I) + (XVIa) (1:10)	2.5 + 25	found 59	calc.*) 21
(I) + (XVIb) (1:10)	2.5 + 25	52	21
(I) + (XXIV) (1:5)	2.5 + 12.5	50	21
(I) + (XVIII) (1:5)	2.5 + 12.5	63	21

Table 1 (continued)

Sphaerotheca test (cucumber) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %	
(I) + (XV) (1:5)	2.5 + 12.5	50	21
(I) + (VIII) (1:5)	2.5 + 12.5	75	21
(I) + (XI) (1:5)	2.5 + 12.5	found 54	calc.*) 21
(I) + (XIII) (1:5)	0.5 + 2.5	80	57
(I) + (XII) (1:5)	0.5 + 2.5	75	59

Table 1 (continued)

Sphaerotheca test (cucumber) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %	
(I) + (IX) (1:5)	2.5 + 12.5	66	31
(I) + (IIc) (1:1)	2.5 + 2.5	90	21
(I) + (III) (1:1)	2.5 + 2.5	85	61
(I) + (IIa) (1:1)	2.5 + 2.5	found 90	calc.*) 50
(I) + (IIb) (1:1)	2.5 + 2.5	93	84

Table 1 (continued)

Sphaerotheca test (cucumber) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %	
(I) + (XIV) (1:1)	2.5 + 2.5	70	38
(I) + (X) (1:1)	2.5 + 2.5	52	21

found = efficacy found

calc. = efficacy calculated using the Colby formula

Example 2

Venturia test (apple) / protective

Solvent: 47 parts by weight of acetone

Emulsifier: 3 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

To test for protective activity, young plants are sprayed with the active compound preparation at the stated application rate. After the spray coating has dried on, the plants are inoculated with an aqueous konidia suspension of the causative organism of apple scab Venturia inaequalis and then remain in an incubation cabin at about 5   20°C and 100% relative atmospheric humidity for one day.
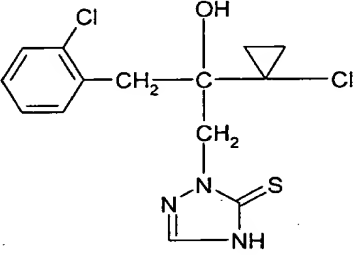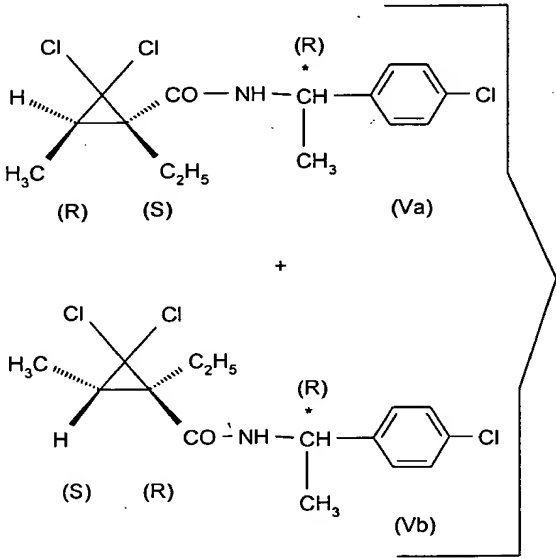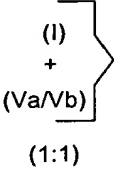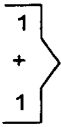
The plants are then placed in a greenhouse at about 21°C and a relative atmospheric humidity of about 90%.

10   Evaluation is carried out 12 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

Active compounds, application rates and test results are shown in the table below.

Table 2

Venturia test (apple) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: Cl—(benzene)—CH₂—C(OH)(cyclopropyl)—Cl with CH₂ linked to N of triazole-thione (I)	1	1
(Va) Cl, Cl, H, H₃C (R), C₂H₅ (S) cyclopropane—CO—NH—CH(CH₃)(R*)—(benzene)—Cl + (Vb) Cl, Cl, H₃C (S), C₂H₅, H (R) cyclopropane—CO—NH—CH(CH₃)(R*)—(benzene)—Cl (1:1 mixture)	1	0
According to the invention: (I) + (Va/Vb) (1:1)	1 + 1	found calc.*) 54 1

found =   efficacy found

calc. =   efficacy calculated using the Colby formula

Example 3

Erysiphe test (barley) / curative

5 Solvent: 10 parts by weight of N-methyl-pyrrolidone

Emulsifier: 0.6 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of
10 solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

To test for curative activity, young plants are dusted with spores of Erysiphe graminis
15 f.sp. hordei. 48 hours after the inoculation, the plants are sprayed with the active compound preparation at the stated application rate.

The plants are placed in a greenhouse at a temperature of about 20°C and a relative atmospheric humidity of about 80% to promote the development of mildew pustules.
20

Evaluation is carried out 7 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

25 Active compounds, application rates and test results are shown in the table below.

Table 3

Erysiphe test (barley) / curative

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	25	81
(XIV)	25	75
According to the invention: (I) + (XIV) (1:3)	6.25 + 18.75	100

Example 4

Erysiphe test (barley) / protective

Solvent: 10 parts by weight of N-methyl-pyrrolidone

Emulsifier: 0.6 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

To test for protective activity, young plants are sprayed with the active compound preparation at the stated application rate.

After the spray coating has dried on, the plants are dusted with spores of Erysiphe graminis f.sp. hordei.

The plants are placed in a greenhouse at a temperature of about 20°C and a relative atmospheric humidity of about 80% to promote the development of mildew pustules.

Evaluation is carried out 7 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

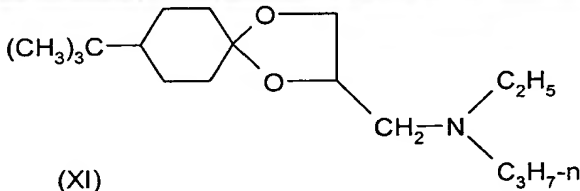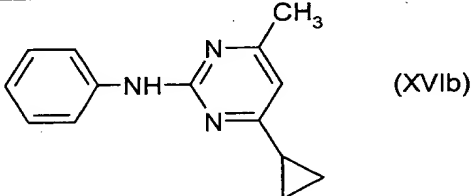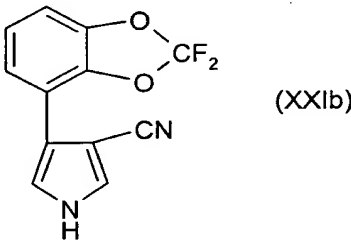Active compounds, application rates and test results are shown in the table below.

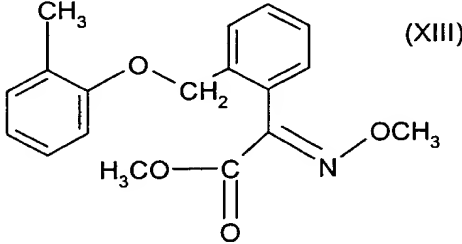**Table 4**

Erysiphe test (barley) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	25	83
(XII)	25	92
According to the invention: (I) + (XII) (1:1)	12.5 + 12.5	100
(I) + (XII) (1:3)	6.25 + 18.75	100
(I) + (XII) (3:1)	18.75 + 6.25	100

Example 5

Erysiphe test (wheat) / curative

Solvent:	10 parts by weight of N-methyl-pyrrolidone
Emulsifier:	0.6 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

To test for curative activity, young plants are dusted with spores of Erysiphe graminis f.sp. tritici. 48 hours after the inoculation, the plants are sprayed with the active compound preparation at the stated application rate.

The plants are then placed in a greenhouse at a temperature of about 20°C and a relative atmospheric humidity of about 80% to promote the development of mildew pustules.

Evaluation is carried out 7 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

Active compounds, application rates and test results are shown in the table below.

Table 5

Erysiphe test (wheat) / curative

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	25 12.5 6.25	75 50 25
 (III)	25	88
 (IIb)	25	81
 (XIV)	12.5	0

Table 5 (continued)

Erysiphe test (wheat) / curative

Active compound	Active compound application rate in g/ha	Efficacy in %
(CH₃)₃C — [cyclohexane-dioxolane ring] CH₂—N(C₂H₅)(C₃H₇-n) (XI)	12.5	0
[phenyl]-NH-[pyrimidine with CH₃ and cyclopropyl] (XVIb)	12.5	0
[benzodioxole-CF₂ with pyrrole-CN] (XXIb)	6.25	38
[CH₃-phenyl-O-CH₂-phenyl methoxyimino acetate] (XIII)	6.25	94
According to the invention: (I) + (III) (1:1)	12.5 + 12.5	100

Table 5 (continued)

Erysiphe test (wheat) / curative

Active compound	Active compound application rate in g/ha	Efficacy in %
(I) + (III) (1:3)	6.25 + 18.75	100
(I) + (III) (3:1)	18.75 + 6.25	100
(I) + (IIb) (1:1)	12.5 + 12.5	100
(I) + (IIb) (1:3)	6.25 + 18.75	100
(I) + (XIV) (1:1)	6.25 + 6.25	63
(I) + (XIV) (3:1)	9.375 + 3.125	75

Table 5 (continued)

Erysiphe test (wheat) / curative

Active compound	Active compound application rate in g/ha	Efficacy in %
(I) + (XI) (1:1)	6.25 + 6.25	100
(I) + (XI) (1:3)	3.125 + 9.375	100
(I) + (XI) (3:1)	9.375 + 3.125	100
(I) + (XVIb) (1:1)	6.25 + 6.25	75
(I) + (XXIb) (1:3)	1.5625 + 4.6875	50
(I) + (XIII) (1:1)	3.125 + 3.125	100

Table 5   (continued)

Erysiphe test (wheat) / curative

Active compound	Active compound application rate in g/ha	Efficacy in %
(I) + (XIII) (1:3)	1.5625 + 4.6875	100

Example 6

Erysiphe test (wheat) / protective

5   Solvent: 10 parts by weight of N-methyl-pyrrolidone

Emulsifier: 0.6 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of
10 solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

To test for protective activity, young plants are dusted with spores of Erysiphe
15 graminis f.sp. tritici.

The plants are then placed in a greenhouse at a temperature of about 20°C and a relative atmospheric humidity of about 80% to promote the development of mildew pustules.
20

Evaluation is carried out 7 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

25 Active compounds, application rates and test results are shown in the table below.

Table 6

Erysiphe test (wheat) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	6.25	57
(III)	6.25	57
According to the invention: (I) + (III) (1:1)	3.125 + 3.125	79
(I) + (III) (1:3)	1.5625 + 4.6875	71
(I) + (III) (3:1)	4.6875 + 1.5625	71

Example 7

Leptosphaeria nodorum test (wheat) / protective

5   Solvent: 10 parts by weight of N-methyl-pyrrolidone

Emulsifier: 0.6 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of 10   solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

To test for protective activity, young plants are sprayed with the active compound 15   preparation at the stated application rate.

After the spray coating has dried on, the plants are sprayed with a spore suspension of Leptosphaeria nodorum. The plants remain in an incubation cabin at 20°C and 100% relative atmospheric humidity for 48 hours.

20

The plants are then placed in a greenhouse at a temperature of about 15°C and a relative atmospheric humidity of about 80%.

Evaluation is carried out 10 days after the inoculation. 0% means an efficacy which 25   corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

Active compounds, application rates and test results are shown in the table below.

Table 7

Leptosphaeria nodorum test (wheat) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	25	62
(XIV)	25	87
According to the invention: (I) + (XIV) (1:3)	6.25 + 18.75	100

Example 8

Puccinia test (wheat) / protective

5 Solvent:	10 parts by weight of N-methyl-pyrrolidone
Emulsifier:	0.6 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of

10 solvent and emulsifier, and the concentrate is diluted with water to the desired concentration, or a commercial formulation of active compound or active compound combination is diluted with water to the desired concentration.

To test for protective activity, young plants are inoculated with a spore suspension of

15 Puccinia recondita in a 0.1% strength aqueous agar solution. After the spray coating had dried on, the plants are sprayed with the active compound preparation at the stated application rate.

The plants remain in an incubation cabin at 20°C and 100% relative atmospheric
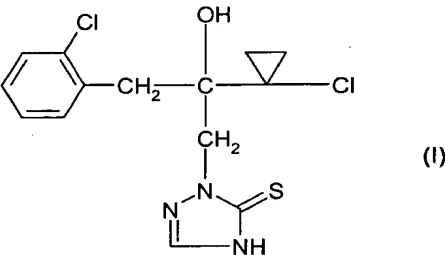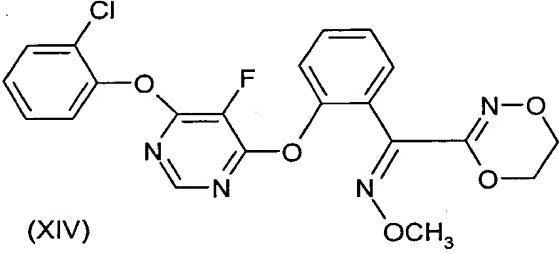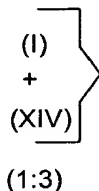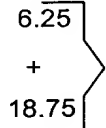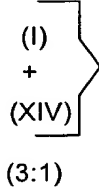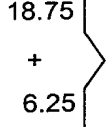
20 humidity for 24 hours.

The plants are then placed in a greenhouse at a temperature of about 20°C and a relative atmospheric humidity of about 80% to promote the development of rust pustules.

25

Evaluation is carried out 10 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

30 Active compounds, application rates and test results are shown in the table below.

Table 8

Puccinia test (wheat) / protective

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	25	38
(XIV)	25	94
According to the invention: (I) + (XIV) (1:3)	6.25 + 18.75	100
(I) + (XIV) (3:1)	18.75 + 6.25	100

Example 9

Fusarium culmorum test (wheat) / seed treatment

5　　The active compounds are applied as a dry seed dressing. This is prepared by extending the respective active compound or the active compound combination with ground minerals to give a finely pulverulent mixture which ensures uniform distribution on the seed surface.

10　　To dress the seed, the infected seed together with the seed dressing is shaken for 3 minutes in a sealed glass flask.

　　2 x 100 corns of wheat are sown at a depth of 1 cm in standard soil and cultivated in a greenhouse at a temperature of about 18°C and a relative atmospheric humidity of

15　　about 95% in seed trays which receive a light regimen of 15 hours per day.
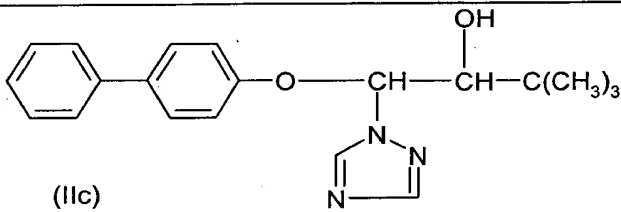
　　About 3 weeks after sowing, the plants are evaluated for symptoms. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

20
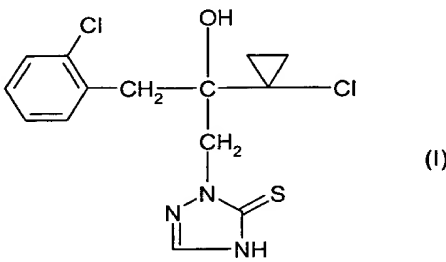
　　Active compounds, application rates and test results are shown in the table below.

Table 9

Fusarium culmorum test (wheat) / seed treatment

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	75	32
 (IIc)	75	27
According to the invention: (I) + (IIc) (1:1)	37.5 + 37.5	41

Example 10

Fusarium nivale test (triticale) / seed treatment

5   The active compounds are applied as a dry seed dressing. This is prepared by extending the respective active compound or the active compound combination with ground minerals to give a finely pulverulent mixture which ensures uniform distribution on the seed surface.

10   To dress the seed, the infected seed together with the seed dressing is shaken for 3 minutes in a sealed glass flask.

2 x 100 corns of wheat are sown at a depth of 1 cm in standard soil and cultivated in a greenhouse at a temperature of about 10°C and a relative atmospheric humidity of 15   about 95% in seed trays which receive a light regimen of 15 hours per day.
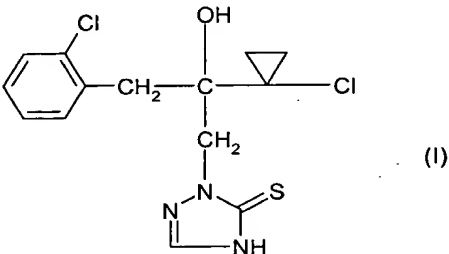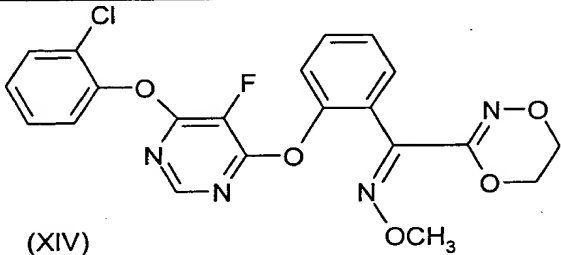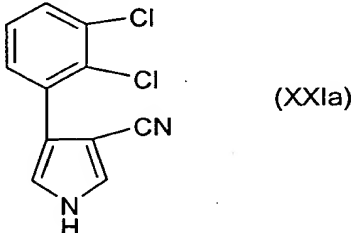
About 3 weeks after sowing, the plants are evaluated for symptoms. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

20

Active compounds, application rates and test results are shown in the table below.

Table 10

Fusarium nivale test (triticale) / seed treatment

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	75 25	14 0
(XIV)	75	94
(XXIa)	25	0
According to the invention: (I) + (XIV) (1:1)	37.5 + 37.5	99
(I) + (XXIa) (1:1)	12.5 + 12.5	31

Example 11

Rhizoctonia solani test (cotton) / seed treatment

5   The active compounds are applied as a dry seed dressing. This is prepared by extending the respective active compound or the active compound combination with ground minerals to give a finely pulverulent mixture which ensures uniform distribution on the seed surface.

10   To dress the seed, the infected seed together with the seed dressing is shaken for 3 minutes in a sealed glass flask.

2 x 50 corns of seed are sown at a depth of 2 cm in standard soil infected with Rhizoctonia solani, and the seeds are cultivated in a greenhouse at a temperature of

15   about 22°C in seed trays which receive a light regimen of 15 hours per day.

Evaluation is carried out after 8 days. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

20   Active compounds, application rates and test results are shown in the table below.

**Table 11**

Rhizoctonia solani test (cotton) / seed treatment

Active compound	Active compound application rate in g/ha	Efficacy in %
Known: (I)	25	19
 (III)	25	27
 (IIc)	25	0
According to the invention: (I) + (III) (1:1)	12.5 + 12.5	40
(I) + (IIc) (1:1)	12.5 + 12.5	31

Patent claims

1. Fungicidal compositions, characterized in that they contain an active compound combination comprising
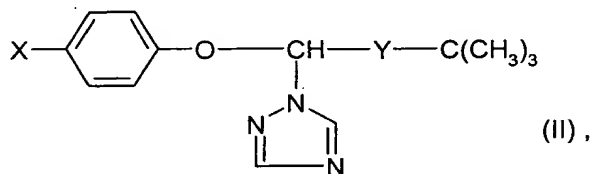
5

2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione of the formula

(I)
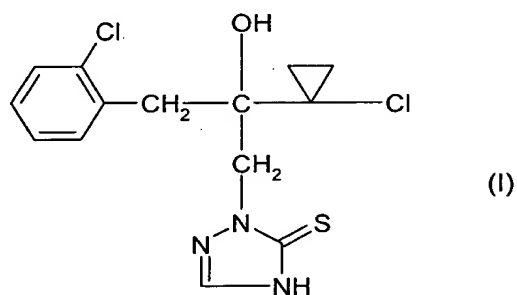
10

and

(1) a triazole derivative of the formula

(II) ,
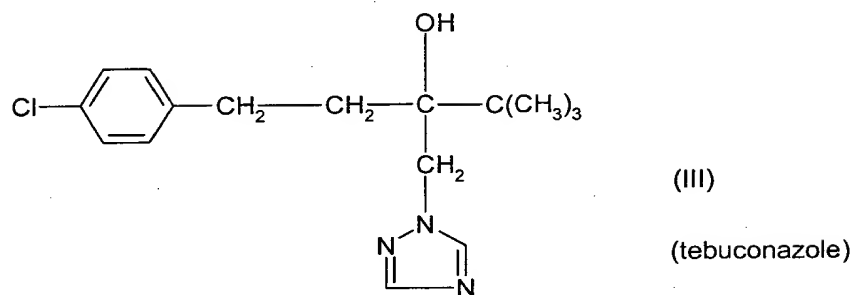
15

in which

X represents chlorine or phenyl

20

and

Y represents $-\overset{\overset{\textstyle O}{\|}}{C}-$ or $-\overset{\overset{\textstyle }{}}{\underset{\textstyle OH}{C}}H-$,

and/or

(2)   the triazole derivative of the formula

$$Cl-\langle C_6H_4 \rangle -CH_2-CH_2-\underset{\underset{CH_2}{|}}{\overset{\overset{OH}{|}}{C}}-C(CH_3)_3$$

(III)

(tebuconazole)

and/or

(3)   an aniline derivative of the formula

$$R^1-\langle C_6H_4 \rangle -N\underset{SO_2-N(CH_3)_2}{\overset{S-CCl_2F}{<}}$$
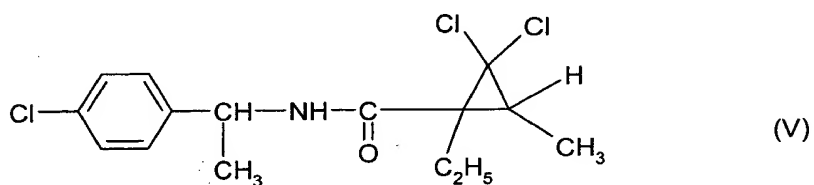
(IV)

in which

R^1 represents hydrogen or methyl,

and/or

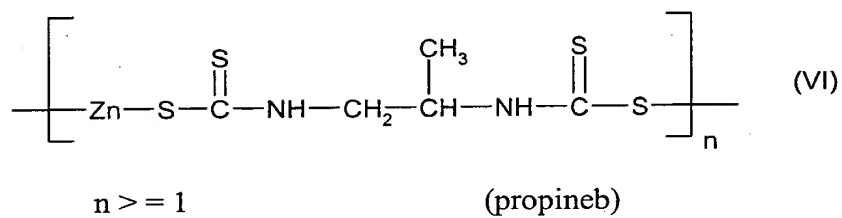(4)   N-[1-(4-chloro-phenyl)-ethyl]-2,2-dichloro-1-ethyl-3-methyl-cyclopropane-carboxamide of the formula

$$Cl-\langle C_6H_4 \rangle -\underset{\underset{CH_3}{|}}{CH}-NH-\underset{\underset{O}{||}}{C}-\text{cyclopropane}(Cl,Cl,H,CH_3,C_2H_5)$$

(V)

and/or

(5)   the zinc propylene-1,2-bis-(dithiocarbamidate) of the formula

5

$$\left[-\text{Zn}-\text{S}-\overset{\overset{\text{S}}{\|}}{\text{C}}-\text{NH}-\text{CH}_2-\overset{\overset{\text{CH}_3}{|}}{\text{CH}}-\text{NH}-\overset{\overset{\text{S}}{\|}}{\text{C}}-\text{S}-\right]_n \qquad \text{(VI)}$$

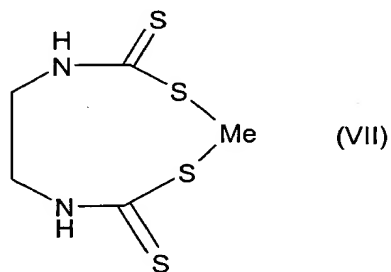n > = 1   (propineb)
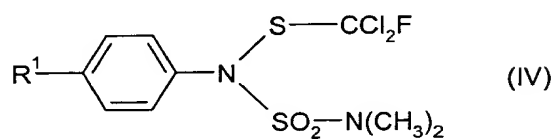
and/or

10

(6)   at least one thiocarbamate of the formula

Me =   Zn or Mn
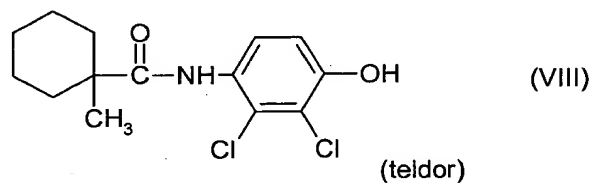
        or a mixture of Zn and Mn

15

and/or

(7)   the aniline derivative of the formula

20

(teldor)
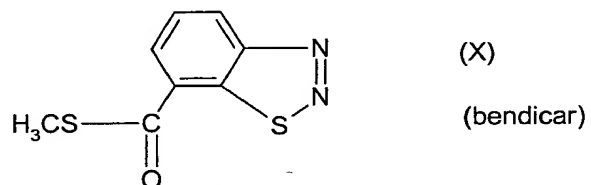
and/or

(8)   the compound of the formula

$$(CH_3)_2CH-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-\overset{\overset{\displaystyle CH(CH_3)_2}{|}}{CH}-\overset{\overset{\displaystyle}{C}}{\underset{\displaystyle O}{\|}}-NH-\overset{\overset{\displaystyle}{CH}}{\underset{\displaystyle CH_3}{|}}\!-\!\!\!\left\langle\right\rangle\!\!-CH_3 \qquad (IX)$$

5

and/or

(9)   the benzothiadiazole derivative of the formula

10

$$H_3CS-\overset{\overset{\displaystyle}{C}}{\underset{\displaystyle O}{\|}}\!\!-\!\!\left[\text{benzothiadiazole ring}\right] \qquad (X)$$

(bendicar)

and/or

15   (10)   the   8-t-butyl-2-(N-ethyl-N-n-propyl-amino)-methyl-1,4-dioxaspiro-
[5,4]-decane of the formula

$$(CH_3)_3C-\!\!\left[\text{dioxaspiro ring}\right]\!\!-CH_2\!\!-\!N\!\!\overset{\displaystyle C_2H_5}{\underset{\displaystyle C_3H_7\text{-n}}{\diagup}} \qquad (XI)$$

(spiroxamine)

20

and/or

(11) the compound of the formula

(XII)

(azoxystrobin)

5 and/or

(12) the compound of the formula

(XIII)

(kresoxim-methyl)
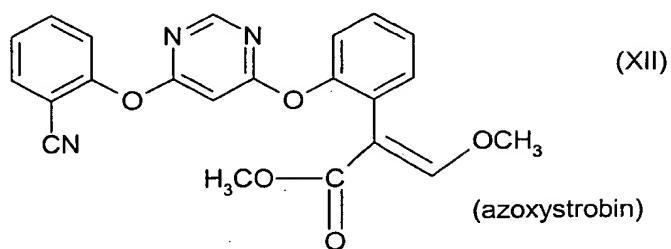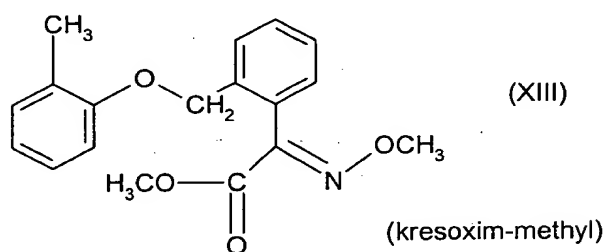
10

and/or

(13) the compound of the formula

(XIV)
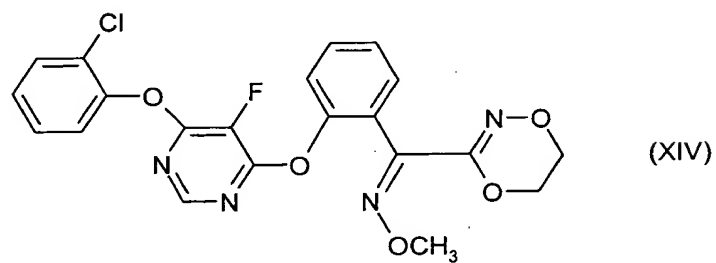
15

and/or

(14) the dicarboximide of the formula

(XV)

(procymidone)

and/or

(15) a pyrimidine derivative of the formula

(XVI)
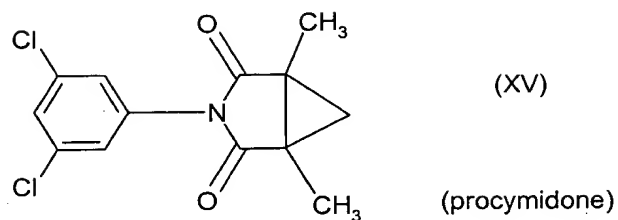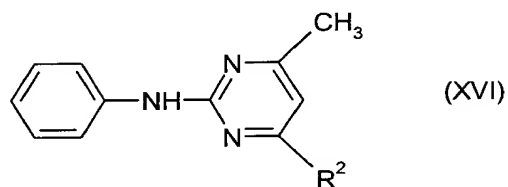
in which

R^2 represents methyl or cyclopropyl,
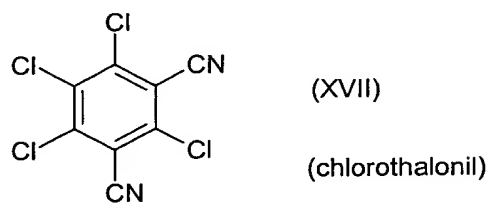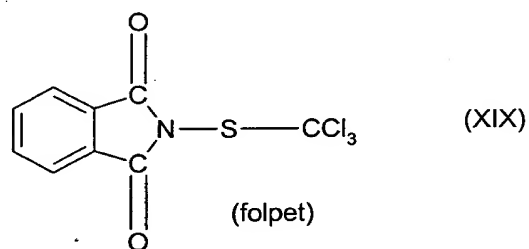
and/or

(16) the phenyl derivative of the formula

(XVII)

(chlorothalonil)

and/or

(17) the morpholine derivative of the formula

(XVIII)

(dimetomorph)

and/or

5

(18)   the phthalimide derivative of the formula

(XIX)

(folpet)

10   and/or

(19)   the phosphorus compound of the formula

Al   (XX)

(fosetyl-Al)

15

and/or

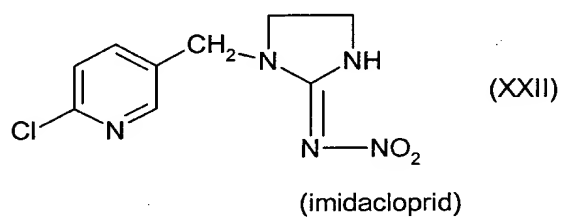(20)   a phenylpyrrole derivative of the formula

(XXI)

in which

R^3 and R^4 each represent chlorine or together represent a radical of the

5   formula -O-CF$_2$-O-,
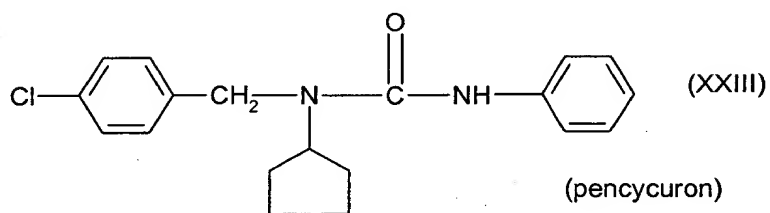
and/or

(21)   the 1-[(6-chloro-3-pyridinyl)-methyl]-N-nitro-2-imidazolidineimine of
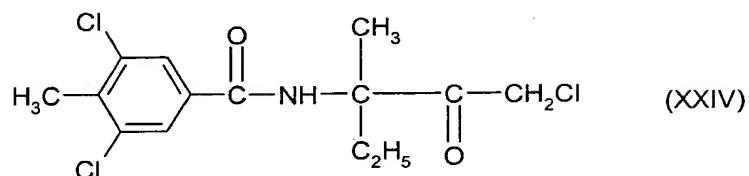
10   the formula

(XXII)

(imidacloprid)

and/or

15

(22)   the phenylurea derivative of the formula

(XXIII)

(pencycuron)

and/or

20

(23)   the benzamide derivative of the formula

(XXIV)

5   and/or

(24)   a guanidine derivative of the formula

$$x \ (2+m) \ CH_3COOH$$

10
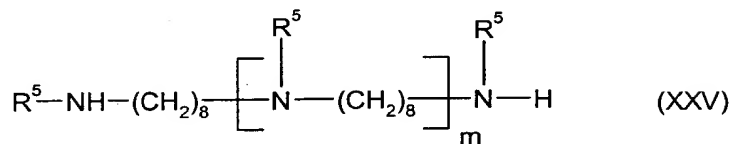
in which

m   represents integers from 0 to 5

15

and

R^5 represents hydrogen (17 to 23 %) or the radical of the formula

(77 to 83 %)

20

2.   Composition according to Claim 1, characterized in that in the active compound combinations the weight ratio of active compound of the formula (I) to

25

- active compound of group (1) is between 1:0.1 and 1:20,

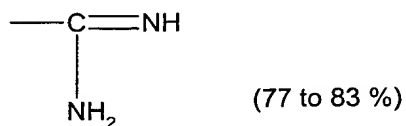- active compound of group (2) is between 1:0.1 and 1:20,

- active compound of group (3) is between 1:0.2 and 1:150,

- active compound of group (4) is between 1:0.1 and 1:10,

5 - active compound of group (5) is between 1:1 and 1:50,

- active compound of group (6) is between 1:1 and 1:50,

- active compound of group (7) is between 1:0.1 and 1:50,

- active compound of group (8) is between 1:0.2 and 1:50,

- active compound of group (9) is between 1:0.02 and 1:50,

10 - active compound of group (10) is between 1:0.1 and 1:50,

- active compound of group (11) is between 1:0.1 and 1:50,

- active compound of group (12) is between 1:0.1 and 1:50,

- active compound of group (13) is between 1:0.1 and 1:50,

- active compound of group (14) is between 1:0.1 and 1:50,

15 - active compound of group (15) is between 1:0.1 and 1:50,

- active compound of group (16) is between 1:1 and 1:50,

- active compound of group (17) is between 1:1 and 1:20,

- active compound of group (18) is between 1:1 and 1:50,

- active compound of group (19) is between 1:1 and 1:50,

20 - active compound of group (20) is between 1:0.1 and 1:10,

- active compound of group (21) is between 1:0.05 and 1:20,

- active compound of group (22) is between 1:0.1 and 1:10,

- active compound of group (23) is between 1:0.1 and 1:10 and

- active compound of group (24) is between 1:0.1 and 1:10.

25

3. Method for controlling fungi, characterized in that active compound combinations according to Claim 1 are applied to the fungi and/or their habitat.

30 4. Use of active compound combinations according to Claim 1 for controlling fungi.

5.   Process for preparing fungicidal compositions, characterized in that active compound combinations according to Claim 1 are mixed with extenders and/or surfactants.

Fungicidal active compound combinations

A b s t r a c t

The novel active compound combinations comprising 2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-2,4-dihydro-[1,2,4]-triazole-3-thione   of   the formula

(I)
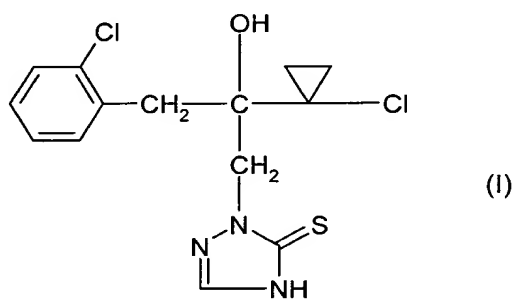
and the active compound of groups (1) to (24) listed in the description have very good fungicidal properties.